

**FORMALDEHYDE SCAVENGERS FOR CLEANER PRODUCTION: A CASE
STUDY FOCUSED ON THE LEATHER INDUSTRY**

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HIGHLIGHTS

- Formaldehyde must be restricted due to its proven impact on humans and eco-systems
- Scavengers reduce at different extent the formaldehyde content in leather
- Hydroxylamine is environmentally toxic and its scavenging ability lowers with time
- Pyrogallol has a high reduction ability but its use results in leather darkening
- Gallic acid may be a good alternative as formaldehyde scavenger

Abstract

Due to its carcinogenic character, the presence of formaldehyde in leather continues to be a subject of great concern. By using formaldehyde scavengers, it is possible to reduce the formaldehyde content in leather. In this work, the potential ability of three different compounds (ethylene urea, pyrogallol and gallic acid) to reduce the formaldehyde content in splits leathers treated with formaldehyde resins (melamine-formaldehyde and dicyandiamide-formaldehyde) is assessed. This capacity is compared with that of a fourth scavenger (hydroxylamine sulphate) already used in tanneries. The evolution of the formaldehyde content with time is also considered, as well as the potential coadjuvant effect of other compounds such as mimosa extract and an acid dye (Acid Black 234). Hydroxylamine sulphate initially showed the highest ability to reduce formaldehyde content. However, after a certain time, this ability proved to be inferior to the ability of other compounds due to the reversibility of the reaction between hydroxylamine and formaldehyde. Pyrogallol showed a higher ability than gallic acid when used in the final wash of leather processing. However, the treatment with pyrogallol results in a darkening of the leather; this darkening limits its use. Gallic acid may be a good alternative to formic acid as the final fixing agent in leather processing when the presence of formaldehyde in leathers is suspected. The use of gallic acid in the final wash or as a fixing agent fulfills the formaldehyde content limit (65-75 mg/kg) of the major brands in leather goods in direct contact with the skin. The addition of 2% of gallic acid in the final wash of leather processing resulted in formaldehyde content reductions that varied from 65% to 85%. However, further experiments are required to assess the influence of gallic acid on the fastness properties and the coloration acquired by the treated leathers. The joint effect of gallic acid in the final wash or as a fixing agent and mimosa extract as a retanning agent in formaldehyde content reduction is even enhanced by subsequently using a dye with amino groups in its chemical structure. Reducing the formaldehyde content by using scavengers can contribute to the achievement of a cleaner production in those sectors (leather, textile, wood) that use formaldehyde resins.

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ABSTRACT

Due to its carcinogenic character, the presence of formaldehyde in leather continues to be a subject of great concern. By using formaldehyde scavengers, it is possible to reduce the formaldehyde content in leather. In this work, the potential ability of three different compounds (ethylene urea, pyrogallol and gallic acid) to reduce the formaldehyde content in splits leathers treated with formaldehyde resins (melamine-formaldehyde and dicyandiamide-formaldehyde) is assessed. This capacity is compared with that of a fourth scavenger (hydroxylamine sulphate) already used in tanneries. The evolution of the formaldehyde content with time is also considered, as well as the potential coadjuvant effect of other compounds such as mimosa extract and an acid dye (Acid Black 234). Hydroxylamine sulphate initially showed the highest ability to reduce formaldehyde content. However, after a certain time, this ability proved to be inferior to the ability of other compounds due to the reversibility of the reaction between hydroxylamine and formaldehyde. Pyrogallol showed a higher ability than gallic acid when used in the final wash of leather processing. However, the treatment with pyrogallol results in a darkening of the leather; this darkening limits its use. Gallic acid may be a good alternative to formic acid as the final fixing agent in leather processing when the presence of formaldehyde in leathers is suspected. The use of gallic acid in the final wash or as a fixing agent fulfils the formaldehyde content limit (65-75 mg/kg) of the major brands in leather goods in direct contact with the skin. The addition of 2% of gallic acid in the final wash of leather processing resulted in formaldehyde content reductions that varied from 65% to 85%. However, further experiments are required to

1 assess the influence of gallic acid on the fastness properties and the coloration acquired
2 by the treated leathers. The joint effect of gallic acid in the final wash or as a fixing
3 agent and mimosa extract as a retanning agent in formaldehyde content reduction is
4 even enhanced by subsequently using a dye with amino groups in its chemical structure.
5 Reducing the formaldehyde content by using scavengers can contribute to the
6 achievement of a cleaner production in those sectors (leather, textile, wood) that use
7 formaldehyde resins.
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13 *Keywords:* cleaner production; leather, textile, wood industries; formaldehyde resins;
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1. Introduction

The analysis of future trends in leather production emphasizes the introduction of cleaner leather processing technologies (UNIDO, 2010). One of the expected results includes avoiding the presence in the leather of substances from the Restricted Substances Lists (RSL) due to its proven impact on human health and ecosystems (UNIDO Leather Panel, 2010) as well as its use in leather processing. Due to the carcinogenic character of formaldehyde (IARC Monographs, 2012; Dixit et al., 2015), its presence in leather continues to be a subject of great concern.

The worldwide production of leather for footwear in 2014 amounts to 561.1 thousand tonnes (FAO, 2016). An estimation of approximately 60%-70% of this production is retanned with resins synthesized with formaldehyde and compounds such as melamine, dicyandiamide and urea. Therefore, a remarkable amount of leather for footwear may pose formaldehyde problems.

According to the results given by the “A3 Chair in Leather Innovation” since 2013 on the formaldehyde content in leather for footwear from Asia, 16% of leathers failed the requirements of most of the major brands (formaldehyde content >75 mg/kg), and for double face skins, this percentage of fails was even higher (approximately 30%) (A3 Chair in Leather Innovation, 2017) as a consequence of retanning with resins of bad quality that either contain an excess of free formaldehyde or are hydrolysed under certain conditions that release formaldehyde (Barret, 1993).

Formaldehyde resins are not only present in the leather industry but also in screen-print inks and in textile finishing. Formaldehyde resins are also applied in many construction materials resulting in one of the more common indoor air pollutants. At concentrations above 0.1 ppm in air, formaldehyde can irritate the eyes and mucous membranes. When inhaled at this concentration, formaldehyde may cause headaches, a burning sensation in the throat, and difficulty breathing, and it can trigger or aggravate asthma symptoms. The emission rate of formaldehyde depends on several factors, the most important of which are ageing and use of additives such as formaldehyde scavengers (Bower, 2001). It is important to continue to be vigilant for new and unexpected sources of allergens from textiles, apparel, and furniture items (Brookstein, 2009).

1 In the literature, different types of formaldehyde scavengers have been reported. For the
2 leather substrate, Bayramoglu et al. (2008) proposed the use of plant extracts (*Vinca*
3 *rosea* and *Camellia sinensis*) for the reduction of free formaldehyde. Unpublished
4 internal studies, carried out by some authors of this work, have shown the possibilities
5 of other compounds, sodium bisulphite or sodium perborate, for the same objective.
6 INESCOP (2012), in addition to these two compounds, extended the study with
7 hydroxylamine sulphate. The application of this compound gave the best formaldehyde
8 content results that were, in most cases, below 150 ppm, the limit established in the
9 current criteria of the European Ecological Label for Footwear. For the wood substrate,
10 the reduction of formaldehyde emitted by medium density fibre panels by the addition
11 of the tannins extracted from the white oak bark (Boran et al., 2012) or different amine
12 compounds (urea, propylamine, methylamine, ethylamine and cyclopentylamine)
13 (Boran et al., 2011) was studied. Costa et al. (2013) evaluated the formaldehyde
14 scavenger capacity of sodium metabisulphite, sodium bisulphite and urea in the
15 adhesive system, consisting of urea-formaldehyde resin and other compounds, for the
16 preparation of wood-based panels. They conclude that the sodium metabisulphite
17 proved to be an excellent scavenger, allowing the production of particleboard panels
18 with zero formaldehyde emission.
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33 In a previous work (Marsal et al., 2017), mimosa extract showed a high capacity to
34 reduce the formaldehyde content of the formaldehyde resin-treated leathers. This
35 capacity, which was accentuated by ageing, is due to the high reactivity of the
36 polyphenols of the mimosa extract towards formaldehyde. Reductions of up to 85% in
37 formaldehyde content after some time of leather processing were obtained by the
38 addition of 4% (on shaved wet-blue weight) of mimosa extract. Therefore, the industrial
39 application of mimosa extract, normally used in tannery in retanning processes, is also
40 beneficial when the presence of formaldehyde is suspected.
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49 Important reductions in the formaldehyde content of formaldehyde resin-treated leathers
50 by the action of adequate scavengers will result in a more sustainable tanning industry
51 not only from the environmental point of view but also from a human health viewpoint,
52 given the carcinogenic character of formaldehyde. This carcinogenic character fully
53 justifies the application of the adequate formaldehyde scavengers in industrial
54 processing of leather, textiles and construction materials.
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The aim of this work is to check the ability of different scavengers not studied so far for reducing the formaldehyde content in leathers treated with resins synthesized with formaldehyde. The evolution of the formaldehyde content with time is also considered. The work is focused on the identification of chemicals that, by their ability as formaldehyde scavengers, enable a more sustainable leather production with chemicals that can also be used as additives in the textile and construction materials industry.

2. Materials and methods

2.1 Materials

2.1.1 Starting material: splits leather

Butts of wet-blue splits of German origin shaved to a thickness of approximately 1.5 mm were the starting material. This material was chosen for its homogeneity. In addition, this thickness facilitates penetration of chemicals in the different treatments performed.

2.1.2 Resins synthesized with formaldehyde

In this work, two resins were employed, one synthesized by the condensation of formaldehyde with melamine and the other with dicyandiamide. These resins are used in the retanning operation of chrome leather to provide adequate properties to the final leather article (Naviglio et al., 2006). However, depending on the scrupulosity in the preparation method, a given amount of free formaldehyde can be found in the resins, which, in addition, are susceptible to hydrolysis, releasing an extra amount of formaldehyde (Barret, 1993). The formaldehyde content \pm 95% confidence interval of the resins employed in this work, which were manufactured in Asia, was melamine-formaldehyde (MF), 23481 ± 369 mg/kg and dicyandiamide-formaldehyde (DCDF), 21216 ± 1000 mg/kg. These experimental results, which are the mean value of five replicates, were determined by applying the method described in Section 2.2.3.

2.1.3 Formaldehyde scavengers

The presence of hydroxyl groups in plant compounds (Marsal et al., 2017) or amino groups in dyes for leather (Marsal et al., in preparation) is of paramount importance in reducing the formaldehyde content of leathers treated with formaldehyde resins. Three chemicals of lower molecular weight not studied so far, also with -OH groups (gallic

acid, Fluka 48630 and pyrogallol, Sigma 16040) or with amino groups (ethylene urea, Sigma-Aldrich 1601) in their structures, have been chosen as possible formaldehyde scavengers for this study. Their ability as scavengers is compared with the ability of the hydroxylamine sulphate, (Trumpler S.A, Spain), a salt consisting of two equivalents of hydroxylamine and one equivalent of sulphuric acid, already used in tanneries. Figure 1 shows the chemical structure of the formaldehyde scavengers studied.

The novelty of the work lies in the possible use of three chemicals (gallic acid, pyrogallol and ethylene urea) not studied so far and in the study of the evolution of the formaldehyde content with time in treated leathers as a function of the scavenger used.

(Figure 1)

2.2 Methods

2.2.1 Processing of leathers. Experiments carried out

The splits received from the tannery (Despell S.A, Igualada) were subjected to the general recipe described in a previous study (Marsal et al., 2017). There were some slight modifications relative to that formulation. The retanning operation was carried out with acrylic resin (3%) and formaldehyde resin (5%). Depending on the experiment, we used MF resin or DCDF resin.

In the first series of experiments, no vegetable compound was added. After fatliquoring, which was carried out exactly as described in that formulation, fixation with formic acid was performed. Finally, the treated splits were washed with 100% water at 45 °C for 45 min, or a 2% solution of each of the formaldehyde scavengers was added to the water in separate experiments.

In the second series of experiments, the work was focused on determining the joint effect of gallic acid, used as formaldehyde scavenger and applied in the final washing as mentioned above, and mimosa extract, which has an excellent ability to reduce formaldehyde content in leathers (Marsal, et al., 2017). The vegetable compound was applied (3%) in the retanning process of leathers treated with MF resin. In the last experiment of this series, this joint effect of gallic acid and mimosa extract was complemented by the application (4%) of Acid Black 234 dye that in previous studies (paper in preparation) also showed a good ability to reduce formaldehyde content in

leather. This dyeing process was performed immediately before the fatliquoring process of the general recipe mentioned above.

In the third series of experiments, gallic acid was not used in the final wash but as a possible alternative to formic acid in the final fixing operation. In addition, a much milder final wash (150% of water at approximately 25 °C for 3 min) was applied instead of the long final wash (100% of water at 45 °C for 45 min) performed in the previous series. Additionally, here, the effect of using or not using mimosa extract was considered. Offers in % are referred to the shaved wet-blue weight.

At the end of all the series of experiments, the treated leathers were air dried. Then, they were analysed after different periods elapsed from the treatments to determine the evolution of the formaldehyde content with time. During the period of analysis, the leather samples were stored under the same conditions of temperature (23 °C) and relative humidity (50%) (EN ISO 2419 Standard, 2012) and placed in airtight plastic bags in the dark.

2.2.2 Analysis of formaldehyde content in leather

The formaldehyde content in splits treated in accordance with the general recipe described in a previous study (Marsal et al., 2017) with the modifications mentioned in Section 2.2.1 was determined following the EN ISO 17226-2 Standard (2008). It was possible to determine the effect of different formaldehyde scavengers in the reduction of the formaldehyde content in splits leathers treated with resins synthesized with formaldehyde.

Some modifications relative to the Standard were applied. In the stage of formaldehyde extraction from the treated splits, sodium dodecyl sulphate was used instead of the much more expensive sodium dodecyl sulphonate (recommended by the Standard). It was confirmed (Cuadros et al., 2016) that both surfactants gave similar results for formaldehyde content in the analysis of the same leathers. Also, in the extraction stage, a reciprocal linear shaker (Selecta, Unitronic) was employed. Previous studies (Cuadros et al., 2016; Manich et al., 2017) have shown that the method used for formaldehyde extraction has great importance to the final results, so it is very important to specify the method used. After filtration, the extracted formaldehyde was spectrophotometrically determined after reaction with acetylacetone in accordance with the Standard.

2.2.3 Analysis of formaldehyde content in formaldehyde resins

An adaptation of the EN ISO 17226-1 Standard (2008) was used to assess the formaldehyde content in the formaldehyde resins employed. The detailed description of the method applied is presented in a previous work (Manich et al., 2017).

2.2.4 Regression analysis

To estimate the evolution of formaldehyde content $[FC]$ as a function of the number of days elapsed after treatment (ND), a linear regression analysis was used for all sets of samples classified in accordance with the formaldehyde resin used and the formaldehyde scavenger added. The initial formaldehyde content, $[FC]_0$, and the rate of change of the content with the number of days (ND) elapsed after treatment, $[FC]_{rate}$, together with the correlation coefficient, r , of the linear regression equation $[FC] = [FC]_0 + [FC]_{rate} \times ND$ are shown in Tables 1-3. These Tables also include the 95% confidence interval of the regression line coefficients. Each formaldehyde content result is the average value of six determinations.

3. Results

3.1 Treatments with MF resin in the retanning operation

Figure 2 shows the formaldehyde content as a function of the number of days elapsed after treatments of splits leathers retanned with MF resin and for four different final washes of the process. The final wash of the process used as control was carried out with only water and in the other three, by adding 2% (on shaved wet-blue weight) of three different formaldehyde scavengers (pyrogallol, ethylene urea and hydroxylamine sulphate) to the water to assess their ability in the reduction of the formaldehyde content. As observed in Figure 2, the three formaldehyde scavengers exhibited a marked ability in the formaldehyde content reduction of splits when compared with the control sample without scavenger.

(Figure 2)

Table 1 shows the linear regression analysis of the formaldehyde content as a function of the number of days elapsed after treatments (see Section 2.2.4).

(Table 1)

The initial reduction ability of hydroxylamine sulphate was higher than the initial reduction ability of pyrogallol and ethylene urea, which showed similar initial reductions $[FC]_0$.

For the sample without scavenger, the formaldehyde content grew slightly with time, although the increase rate was not significant ($+0.08 \pm 0.12$ mg/kg per day elapsed).

The addition of scavengers in the final wash modified the evolution of formaldehyde content with time. The hydroxylamine sulphate caused a drastic reduction of the initial formaldehyde content from 210.19 ± 16.99 mg/kg to 48.75 ± 32.13 mg/kg, although the concentration remained practically constant over time; the slight growing trend ($+0.02 \pm 0.23$ mg/kg per day elapsed) could suggest some reversibility causing formaldehyde release. The pyrogallol and ethylene urea decreased the initial formaldehyde content to 109.54 ± 49.60 mg/kg and 100.16 ± 19.92 mg/kg, respectively, although pyrogallol caused a higher decrease in formaldehyde content per day elapsed after treatment (-0.47 ± 0.35 mg/kg) than the decrease caused by ethylene urea (-0.18 ± 0.14 mg/kg). The influence of pyrogallol on formaldehyde content was significantly different at 5% from the influence of ethylene urea or hydroxylamine sulphate (Mead et al., 2003).

The reduction (in %) of formaldehyde content in leathers washed with scavengers in the final wash relative to leathers washed only with water is given by the following equation:

$$\text{Reduction in formaldehyde content (\%)} = \frac{([FC]_{\text{water}} - [FC]_{\text{water+scavenger}})}{[FC]_{\text{water}}} \times 100$$

[1]

Figure 3 shows the effect of formaldehyde scavengers added to the final wash of leathers retanned with MF resin on the reduction of formaldehyde content as a function of the days elapsed after treatments.

(Figure 3)

The addition of a 2% pyrogallol solution caused the greatest reduction in formaldehyde content when compared with the leather washed only with water. This reduction progressively increased from approximately 30% (7 days after treatments) to

approximately 90% (228 days after treatments). The progressive increase of the formaldehyde content of splits washed only with water (Figure 2) compared with the progressive reduction of splits washed including 2% pyrogallol enhanced the final reduction in the formaldehyde. Concerning the addition of a 2% of ethylene urea, the reduction of the formaldehyde content varied from approximately 44% (7 days after treatments) to approximately 70%, which remained practically constant from 119 days. The addition of hydroxylamine sulphate (2%) caused the highest initial formaldehyde reduction (64% at 7 days after treatments). This reduction continued to increase up to 83% at 91 days. However, from 119 days after treatments, the reduction of the formaldehyde content with respect to the leather washed only with water began to decrease progressively to approximately 69%, which could be caused by a possible reversibility of the scavenger action resulting, after some time, in formaldehyde release.

3.2 Treatments with DCDF resin in the retanning operation

The study with DCDF resin as retanning agent was carried out with two formaldehyde scavengers (pyrogallol and hydroxylamine sulphate) as used with MF resin (Section 3.1) and a new scavenger, 2% gallic acid added to water in the final wash.

By comparing Figures 2 and 4, control samples (without scavenger) retanned with MF resin (Fig. 2) showed higher formaldehyde content than the formaldehyde content shown by the samples retanned with DCDF resin (Fig. 4).

(Figure 4)

As observed in Table 1, the initial formaldehyde content of leathers retanned with MF resin and washed only with water was 210.19 ± 16.99 mg/kg whereas when DCDF resin was used, it was 159.65 ± 14.23 mg/kg. No significant variation in formaldehyde content with time was observed in splits treated with MF resin ($+0.08 \pm 0.12$ mg/kg per day), whereas for those retanned with DCDF resin a growth in formaldehyde content with time was noted ($+0.17 \pm 0.13$ mg/kg per day elapsed after treatments).

The greater effect of pyrogallol and hydroxylamine sulphate in the reduction of formaldehyde content in leathers treated with DCDF resin compared with those treated with MF resin can be explained by the lower formaldehyde content of the DCDF resin. The addition of pyrogallol or hydroxylamine sulphate into the final wash (2%) gave rise to a diminution in the initial formaldehyde content from 159.65 ± 14.23 mg/kg to

10.51±5.99 mg/kg or to 7.46±5.06 mg/kg, respectively. For pyrogallol, because of this important reduction in the formaldehyde content from the beginning, the formaldehyde content remained practically constant over time (-0.01±0.05 mg/kg) while for the hydroxylamine sulphate, the growth observed in formaldehyde content over time was much greater (+0.18±0.05 mg/kg) than for treatments with MF resin (+0.02±0.23 mg/kg). This growth in formaldehyde content with time could confirm a partial reversibility of the action of the hydroxylamine sulphate, resulting in a release of formaldehyde, as noted in Section 3.1. Gallic acid gave rise to a smaller decrease in the initial formaldehyde content than that caused by both pyrogallol and hydroxylamine sulphate (53.77±14.43 mg/kg), although a significant diminution of the formaldehyde content with time was observed (-0.19±0.13 mg/kg per day).

Figure 5 shows the reduction of formaldehyde content with time due to the addition of formaldehyde scavengers into the final wash of leathers retanned with DCDF resin.

(Figure 5)

Greater reductions in formaldehyde content when compared with splits treated with MF resin (Figure 3) were observed, probably due to the lower formaldehyde content of samples treated with DCDF resin. Depending on the scavenger, the maximum reductions were reached at different times: the reduction caused by gallic acid varied from 63% (after 14 days) to 88% (at 202 days). For pyrogallol, the maximum reduction (approximately 96%) was reached at 60 days, remaining practically constant thereafter. For hydroxylamine sulphate, the maximum formaldehyde reduction (92%) was initially achieved (at 14 days) and progressively decreased up to 74% after 202 days of leather processing, explained by the aforementioned partial reversibility of its reaction with formaldehyde.

3.3 Treatments using gallic acid as formaldehyde scavenger

3.3.1 Joint effect of gallic acid, mimosa extract and Acid Black 234 dye

Figure 6 shows the joint effect of gallic acid (applied in the final wash), mimosa extract and Acid Black 234 dye on the formaldehyde content in splits leathers retanned with MF resin. For comparison, the variation of the formaldehyde content with time for leathers treated only with the resin and the effect of adding mimosa extract (3%), which

in a previous work (Marsal et al., 2017) proved to be an excellent alternative to reduce the formaldehyde content in leathers, are presented. Figure 6 also shows the effect of the application of gallic acid (2%) in the final wash of leathers retanned with MF resin and mimosa extracts, on one hand, and further dyed with Acid Black 234 dye, on the other. This dye has been taken as an example of a compound with amino groups in its structure and, thus, to assess, through its reaction with formaldehyde, its influence on the content of formaldehyde in treated leathers.

(Figure 6)

The application of mimosa extract in retanning caused a marked reduction, accentuated with ageing, in formaldehyde content of leathers treated with MF resin. Washing with gallic acid resulted in a much more drastic reduction, and dyeing with Acid Black 234 dye provoked a reduction of the initial formaldehyde content, which was even slightly higher than the initial formaldehyde content of the undyed leathers. Table 2 shows the linear regression analysis of the formaldehyde content as a function of the number of days elapsed after treatments for all the experiments in this series (see Section 2.2.4).

(Table 2)

For the control sample (only treated with MF resin), there was a growth of $+0.24 \pm 0.15$ mg/kg of formaldehyde per day elapsed after treatment, the increase probably due to the progressive hydrolysis of the resin. The application of mimosa extract (3%) resulted in a reduction of the initial formaldehyde content from 206.54 ± 16.52 mg/kg to 177.20 ± 18.45 mg/kg and a decrease of -0.38 ± 0.17 mg/kg of formaldehyde per day elapsed after treatments. Washing with gallic acid caused a much more drastic descent of the initial formaldehyde content up to 81.26 ± 29.62 mg/kg whereas the decrease in the formaldehyde content with time was -0.37 ± 0.27 mg/kg of formaldehyde per day elapsed after treatments. Additional dyeing with Acid Black 234 dye resulted in a more pronounced decrease in the initial formaldehyde content (from 206.54 ± 16.52 mg/kg to 63.52 ± 21.48 mg/kg), whereas the decrease rate per day elapsed after treatment was -0.28 ± 0.19 mg/kg. Differences between the regression equations for splits leathers with or without dyeing with Acid Black 234 dye were not significant (Mead et al., 2003); this outcome led to the conclusion that the most important effect in reducing the formaldehyde content of MF resin treated leathers is that caused by the application of gallic acid applied in the final wash.

Figure 7 shows the evolution with time of the reduction of formaldehyde content (%) in leathers treated with MF resin by the effect of i) addition of mimosa extract in the retanning process, ii) inclusion of gallic acid in the final wash and iii) additional dyeing with Acid Black 234 dye before the final wash with gallic acid relative to leathers treated only with the resin. The % of reduction was obtained by applying Equation [1].

(Figure 7)

The addition of mimosa extract (3%) in the retanning process provoked a reduction in the formaldehyde content from ~ 8% (at 7 days after treatments) to 54.5% (at 217 days after treatments), results similar to those reported in a previous study (Marsal et al., 2017). If leathers were washed with 2% gallic acid, the reduction in formaldehyde content compared with samples treated only with the resin grew considerably from 45% (at 7 days after treatments) to 91% (at 217 days after treatments). This reduction can be considered constant from 73 days after treatments (~90%). If the leathers retanned with mimosa extract were subsequently dyed with Acid Black 234 dye (4%) and finally washed with gallic acid (2%) added to the water, the main effect on the formaldehyde reduction was observed in the analysis performed at 7 days after treatments (~ 60% reduction vs 45% for the undyed leathers). In the subsequent analyses, the % of reduction for dyed and undyed leathers was equalized and was practically similar at 73 days after the treatments (~ 91-92% reduction). The results confirm the predominant effect of washing with gallic acid in the reduction.

3.3.2 Use of gallic acid as a possible alternative to formic acid in the final fixing operation

Figure 8 shows the effect of using gallic acid instead of formic acid in the final fixing operation (see Section 2.2.1) on the formaldehyde content of splits leathers retanned with MF resin. In this case, a milder final wash (150% water at approximately 25 °C for 3 minutes) compared with previous Sections (100% of water at 45 °C for 45 min) was performed. The addition of mimosa extract in the retanning process was also considered. The leather retanned with MF resin and with formic acid in the final fixing operation was taken as the reference. For this treatment and probably due to the progressive hydrolysis of the resin, the formaldehyde content increased over time as reported in a previous study (Marsal et al., 2017) and as mentioned in Section 3.3.1. The ability of mimosa extract in reducing the formaldehyde content was clearly observed.

Figure 8 shows that if formic acid was replaced by gallic acid in the final fixing step of the two treatments, greater reductions in formaldehyde content were attained.

(Figure 8)

Table 3 shows the linear regression equations for all the treatments of this series. The replacement of formic acid by gallic acid as fixing agent caused a diminution in the initial formaldehyde content in leathers retanned with MF resin from 189.55 ± 10.13 mg/kg to 55.70 ± 25.19 mg/kg. The evolution of the formaldehyde content with time varied from a growth of $+0.36 \pm 0.09$ mg/kg per day elapsed after treatments (with formic acid as fixing agent) to remain practically constant (-0.13 ± 0.22 /kg) with gallic acid as fixing agent. The addition of mimosa extract (4%) to the process of the control sample ((MF + Formic Acid (2%)) decreased the initial formaldehyde content from 189.55 ± 10.13 mg/kg to 114.30 ± 12.98 mg/kg with a formaldehyde content rate of -0.26 ± 0.11 mg/kg per day elapsed after treatment, but if gallic acid were used instead of formic acid, the initial formaldehyde content dropped to 27.09 ± 9.33 mg/kg. Given that the reduction rate (-0.05 ± 0.08 mg/kg) was practically zero, the formaldehyde content can be considered to remain constant with time. The addition or lack of addition of mimosa extract (4%) to the retanning process with MF resin and with gallic acid as fixing agent gave rise to a difference between their regression equations that was significant at 5% (Mead et al., 2003).

(Table 3)

Figure 9 shows the reduction of formaldehyde content with time by the effect of gallic acid used as a fixing agent in the treatment of leathers retanned with MF resin and with/without the addition of mimosa extract. Equation 1 was applied to determine the results of formaldehyde content reduction in %.

(Figure 9)

The addition of mimosa extract (4%) caused a reduction in formaldehyde content with respect to the control sample (MF + formic acid as fixing agent) that varied from 36% (at 14 days after treatments) to approximately 74% (at 200 days after treatments). These values of formaldehyde reduction are somewhat higher than the values reported in Section 3.3.1 due to the greater amount of mimosa extract applied (4% instead of 3%). The change in the formic acid by the gallic acid as fixing agent resulted in a reduction

of formaldehyde content that grew from ~60% (at 14 days after treatments) to 85% (from 60 to 200 days after treatments). This reduction was even more pronounced if, together with the effect of fixing with gallic acid, the action of the mimosa extract in the retanning process was considered. In this case, the formaldehyde content reduction varied from ~81% (at 14 days after treatments) to ~91% (at 60 days after treatment), which remained practically constant up to the analyses performed at 200 days after treatments. The effect of gallic acid in reducing the formaldehyde content in splits leathers retanned with MF resin was more intense and occurred more quickly than that of the mimosa extract, probably due to the greater number of –OH groups amenable to reaction with formaldehyde in the gallic acid offered than in the mimosa extract. However, additional experiments are required to confirm this hypothesis.

The significant reduction in the formaldehyde content cannot be attributed to the intensity of the final wash performed in previous sections (100% of water at 45 °C for 45 min) because a milder final wash (150% of water at approximately 25 °C for 3 min) carried out in this series resulted in higher reductions.

4. Discussion

4.1 Influence of scavengers on formaldehyde content of leathers retanned with formaldehyde resins

From the formaldehyde scavengers considered, hydroxylamine sulphate showed the highest capacity to reduce the formaldehyde content in leathers retanned with MF and DCDF resins at short times after leather processing. Other authors (INESCOP, 2012) drew the same conclusion when hydroxylamine sulphate was compared with other scavengers such as sodium bisulphite and sodium perborate. They reported that hydroxylamine sulphate reduced formaldehyde content in 71% and 80% of hides tanned with chromium salts and retanned with MF and DCDF resins, respectively. These results are similar to those obtained in our work. Hydroxylamine owes its sequestering ability to the condensation reaction of –NH₂ groups with formaldehyde resulting in formaldoxime. The reversibility of this reaction (Jolad and Rajagopal, 1966) explains that formaldehyde can be released again. Costa et al. (2013) also noted that the addition reaction between formaldehyde and urea used as scavenger forms methylolureas, which tend to undergo hydrolysis in the presence of moisture, releasing formaldehyde (Dunky, 1998; Pizzi and Mittal, 1994). In our work, the reversibility explains the lower

sequestering capacity of the hydroxylamine sulphate when compared with that of pyrogallol and gallic acid at increasing times after leather processing.

Pyrogallol and gallic acid react with formaldehyde through the -OH groups in their molecules, resulting in a reduction of formaldehyde content in splits retanned with formaldehyde resins. Pyrogallol showed higher reduction ability than gallic acid due to the presence of a deactivating group (carboxylic acid) in the phenolic moiety of the gallic acid (Garro-Gálvez and Riedl, 1997). However, treatment with pyrogallol in the final wash causes a darkening effect on leather, which limits its use.

The “Verwaltungsvorschrift wassergefährdende Stoffe” (the national German regulation on water hazard classification) classifies the hydroxylamine sulphate at the highest class (WGK3) of water hazard (GESTIS Substance database, 2017), and pyrogallol is harmful to the aquatic life with long lasting effects (Sigma Aldrich Statements, 2017). Therefore, the use of both chemicals is not environmentally recommended, in addition to the drawbacks mentioned above.

When the presence of formaldehyde in leather is expected, gallic acid is a good option either in the final washing of the leather production process or as an alternative to formic acid as final fixing agent since it causes a marked reduction in the formaldehyde content. In most of the treatments with gallic acid, the formaldehyde content in the treated leathers was below the limit for goods that are in direct contact with skin (65-75 mg/kg) (Manich et al., 2017). Reductions in formaldehyde content by the addition of 2% of gallic acid in the final wash of leather processing varied from 65% to 85% depending on when the analysis was carried out. Similar reductions in formaldehyde content were reported for hydroxylamine sulphate (INESCOP, 2012). However, gallic acid does not have the drawbacks of toxicity and reversibility of reaction with formaldehyde. According to the safety data sheets, there are no hazard statements for gallic acid (Sigma Aldrich Statements, 2017) from the environmental point of view. Consequently, the application of gallic acid at the industrial scale as an additive to achieve a cleaner production in the leather sector, as well as in other sectors that use formaldehyde resins in their industrial processes (textile and wood sectors), is justified.

A higher reduction in formaldehyde content can be achieved if mimosa extract is included in the retanning process, confirming the ability of mimosa polyphenols to reduce the formaldehyde content of splits leather treated with formaldehyde resins

(Marsal et al., 2017). The application of a dye with amino groups (Acid Black 234) enhances, even more, the reduction in formaldehyde content. These results agree with the results from an unpublished study of the authors (Marsal et al., in preparation). The simultaneous application of gallic acid, mimosa extract and Acid Black 234 dye increases the sites amenable to reaction with formaldehyde (-OH groups in the mimosa extract and gallic acid and -NH₂ groups in the dye) resulting in a formaldehyde content reduction that varied from 60% after 7 days of leather processing to 90% after 90 days elapsed after leather treatments.

For comparison, and being aware of the substrate (medium density fibreboard panels), the method of analysis (perforator method) and the formaldehyde quantified (formaldehyde emitted by the fibreboard panels) are different from those in our study; we present data on the reduction of formaldehyde emitted by these panels bound with urea formaldehyde resin by the action of various amine compounds employed as scavengers (Boran et al., 2011). The authors found that the formaldehyde emission of medium density fibreboard panels produced at a 16% rate of urea-formaldehyde resin decreased 57%, 16.5%, 41% and 48% using 0.8% rate of cyclopentylamine, ethylamine, propylamine and methylamine solution addition, respectively

4.2 Variation with time of formaldehyde content in leathers retanned with formaldehyde resins: Influence of scavengers

The content of formaldehyde in leather retanned with formaldehyde resins increased progressively with time due to the gradual hydrolysis of the resins, which is facilitated by the conditions of the treated leather (humidity level, slightly acidic pH). The reversibility of the reaction between melamine and formaldehyde was previously reported by Barret (1993).

In general, the addition of the scavengers in leathers retanned with formaldehyde resins resulted in a decrease in the formaldehyde content with time, with the exception of hydroxylamine sulphate for the reasons explained in Section 4.1. The -OH and -NH₂ groups of the scavenger react with the free formaldehyde of the leather. This formaldehyde comes from the resin preparation process and/or from the resin hydrolysis. The extent of this reaction is a function of the amount of scavenger in the retanned leathers. The analytical method does not quantify the reacted formaldehyde.

1 Since the resin hydrolyses progressively with time, less unhydrolysed resin can be
2 extracted in the extraction step of the analytical method. The extracted resin
3 (unhydrolysed) is hydrolysed during the analytical method releasing formaldehyde,
4 which is subsequently quantified. If the amount of extracted resin decreases with time,
5 the quantified formaldehyde is also lower. All of this will depend on whether the
6 amount of -OH and -NH₂ groups of scavengers in treated leathers is enough.
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10 11 12 **5. Conclusions** 13

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15 The four chemicals (hydroxylamine sulphate, ethylene urea, pyrogallol and gallic acid)
16 showed formaldehyde scavenging ability in leathers retanned with formaldehyde resins.
17 The lower the formaldehyde content is in the leather, the greater the effectiveness of the
18 applied scavengers.
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23 Hydroxylamine sulphate showed the highest ability to reduce the initial formaldehyde
24 content, although due to the reversibility of its reaction with formaldehyde under acidic
25 conditions (those of the retanning process), its scavenging ability decreased with ageing,
26 being even lower than the scavenging ability of pyrogallol and gallic acid after a certain
27 time. In addition, hydroxylamine sulphate has a high level of toxicity to the aquatic
28 environment with long lasting effects.
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35 Pyrogallol showed a higher ability in reducing the formaldehyde content than gallic
36 acid. However, pyrogallol is harmful to the aquatic life, and its application results in
37 leather darkening. The drawbacks of hydroxylamine sulphate and pyrogallol limit use as
38 formaldehyde scavengers.
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43 The application of gallic acid either in the final wash or as an alternative to formic acid
44 in the final fixing operation of leather processing fulfils the formaldehyde content limit
45 (65-75 mg/kg) of the major brands in leather goods in direct contact with the skin.
46 Therefore, gallic acid is suitable as a formaldehyde scavenger in the leather industry,
47 although further experiments should be carried out to check its effects on fastness
48 properties (mainly to light and temperature) and leather shades.
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55 The joint effect of gallic acid and mimosa extract results in an enhanced formaldehyde
56 content reduction, being even higher if leathers are subsequently dyed with a dye
57 containing amino groups in its structure (e.g., Acid Black 234). Formaldehyde content
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1 reductions ranged from 60% after 7 days to 90% after 90 days elapsed after leather
2 treatments.

3
4 The reduction in formaldehyde content of substrates treated with formaldehyde resins in
5 the leather, textile and wood industries can be attained through the application of gallic
6 acid as a formaldehyde scavenger. The inclusion of additives containing hydroxyl
7 and/or amino groups steps up the formaldehyde content reduction of the substrates. The
8 application of these additives contributes definitively to the achievement of a cleaner
9 production in these industrial sectors.
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Figure Captions

Figure 1. Chemical structure of the formaldehyde scavengers studied.

Figure 2. Formaldehyde content as a function of scavengers in leathers retanned with MF resin.

Figure 3. Reduction of formaldehyde content (%) as a function of the scavengers in leathers retanned with MF resin.

Figure 4. Formaldehyde content as a function of scavengers in leathers retanned with DCDF resin.

Figure 5. Reduction of formaldehyde content (%) as a function of the scavengers in leathers retanned with DCDF resin.

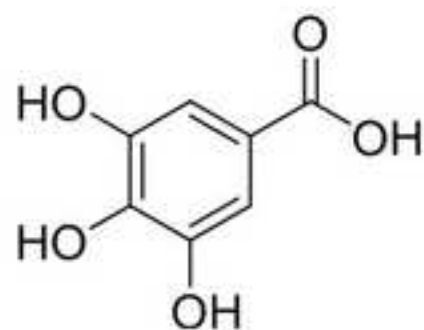
Figure 6. Joint effect of gallic acid, mimosa extract and Acid Black 234 dye on the formaldehyde content in leathers retanned with MF resin.

Figure 7. Reduction of formaldehyde content by the joint effect of gallic acid, mimosa extract and Acid Black 234 dye in leathers retanned with MF resin.

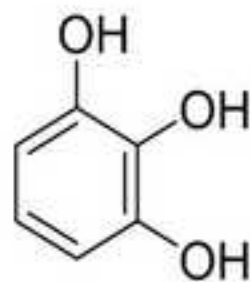
Figure 8. Effect of gallic acid as an alternative to formic acid in the final fixing operation on the formaldehyde content in leathers retanned with MF resin.

Figure 9. Reduction of formaldehyde content (%) as a function of gallic acid as fixing agent in leathers retanned with MF resin.

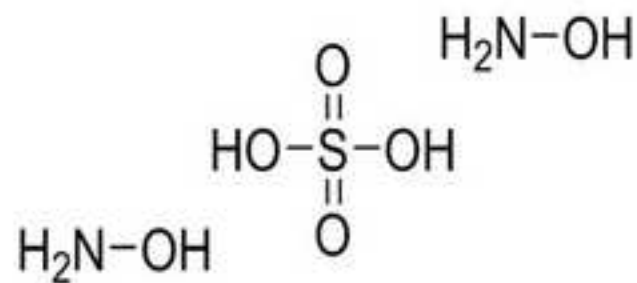
Figure 1
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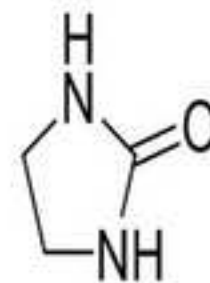
Gallic Acid



Pyrogallol



Hydroxylamine Sulfate



Ethylenurea

Figure 2
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Formaldehyde content (mg/kg)

Formaldehyde content as a function of scavengers

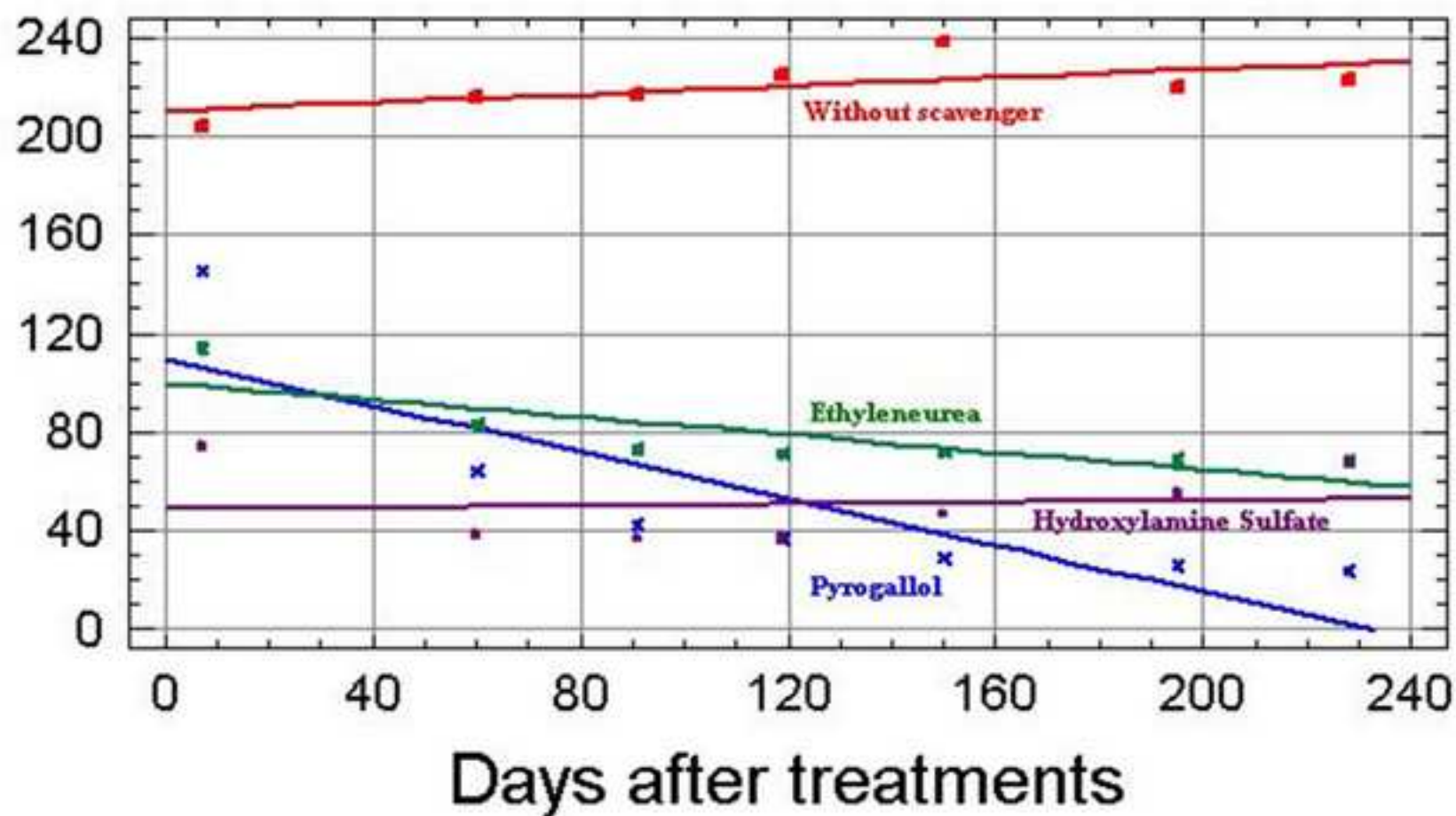


Figure 3
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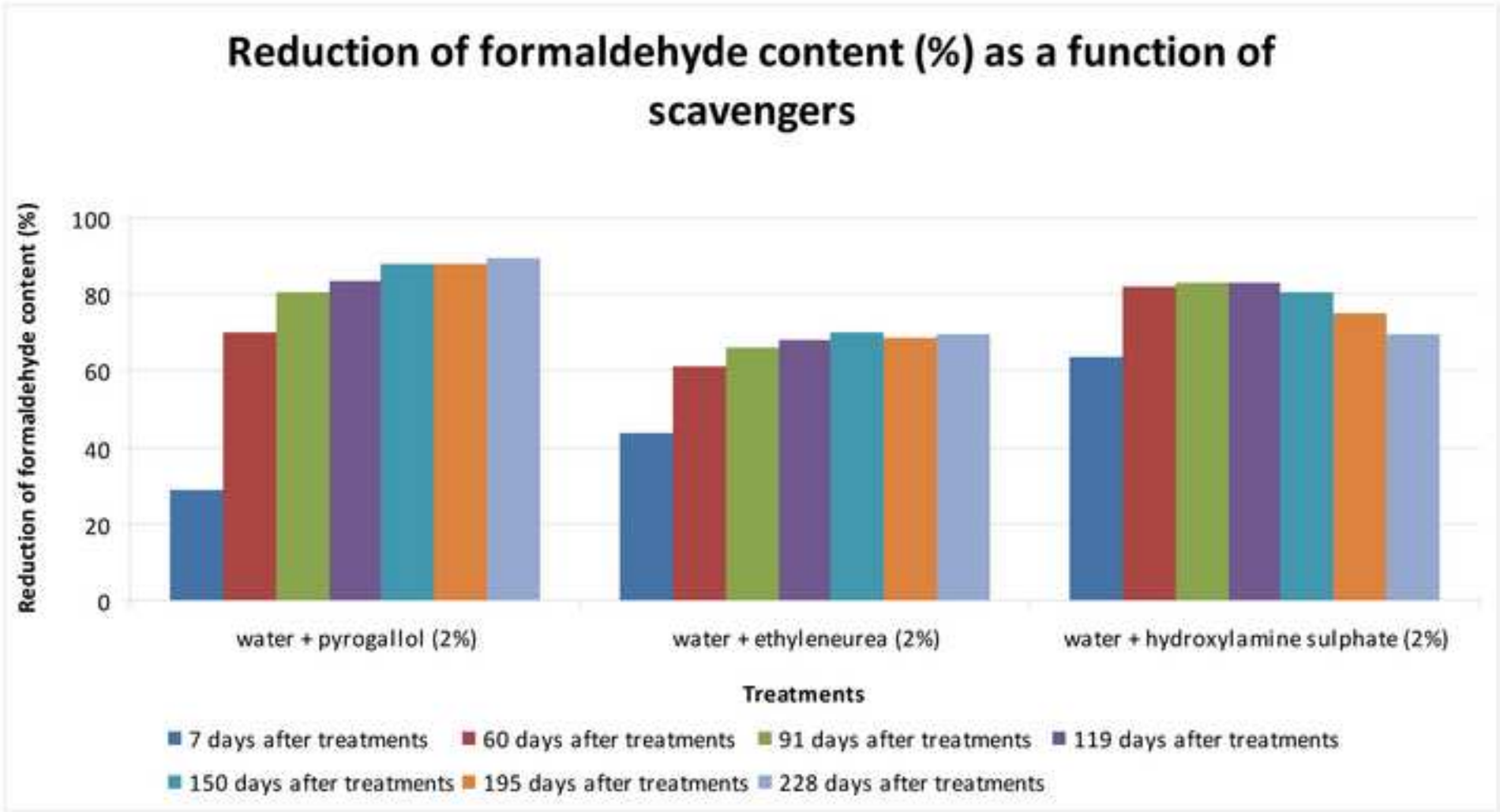


Figure 4
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Formaldehyde content (mg/kg)

Formaldehyde content as a function of scavengers

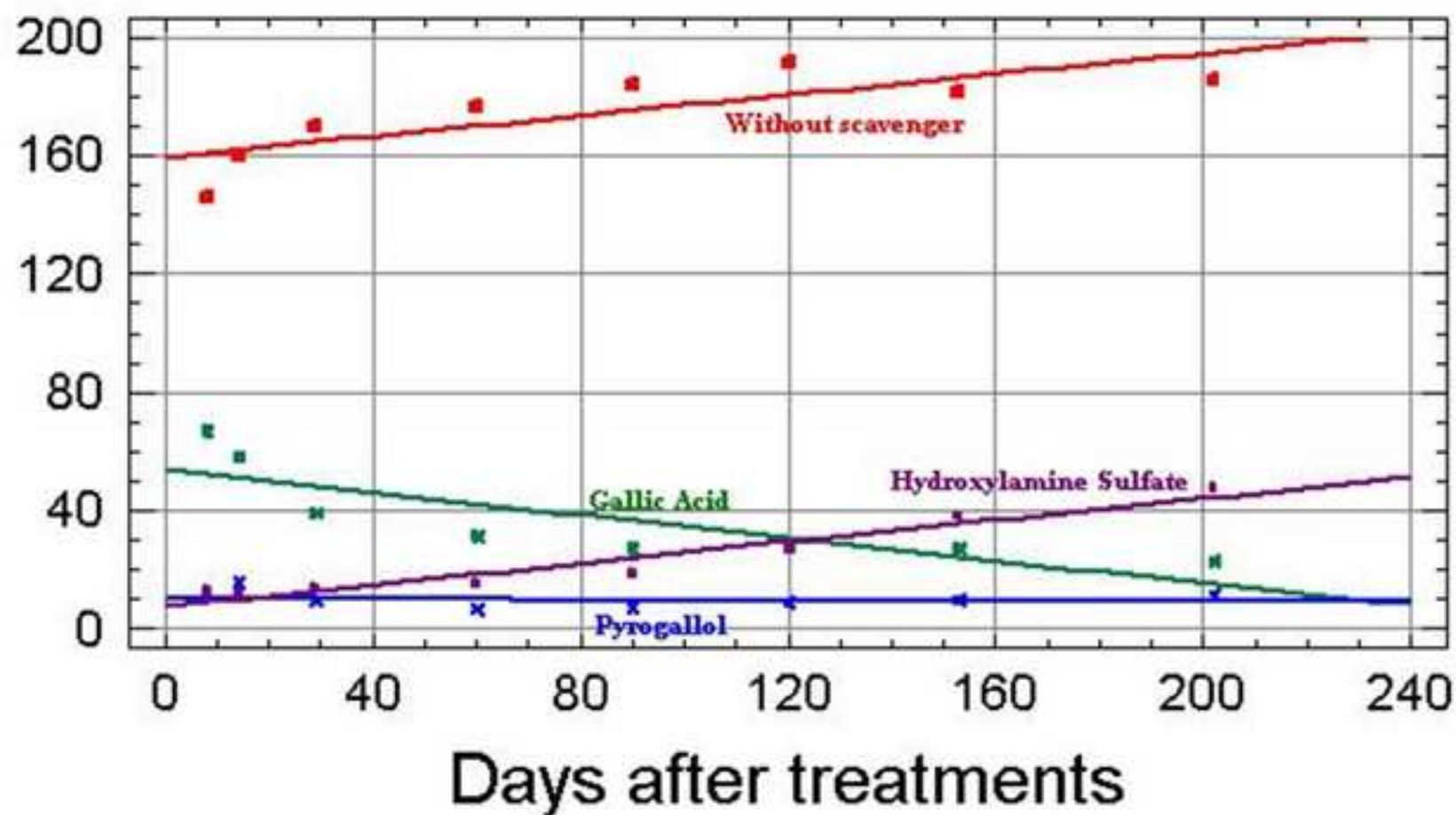


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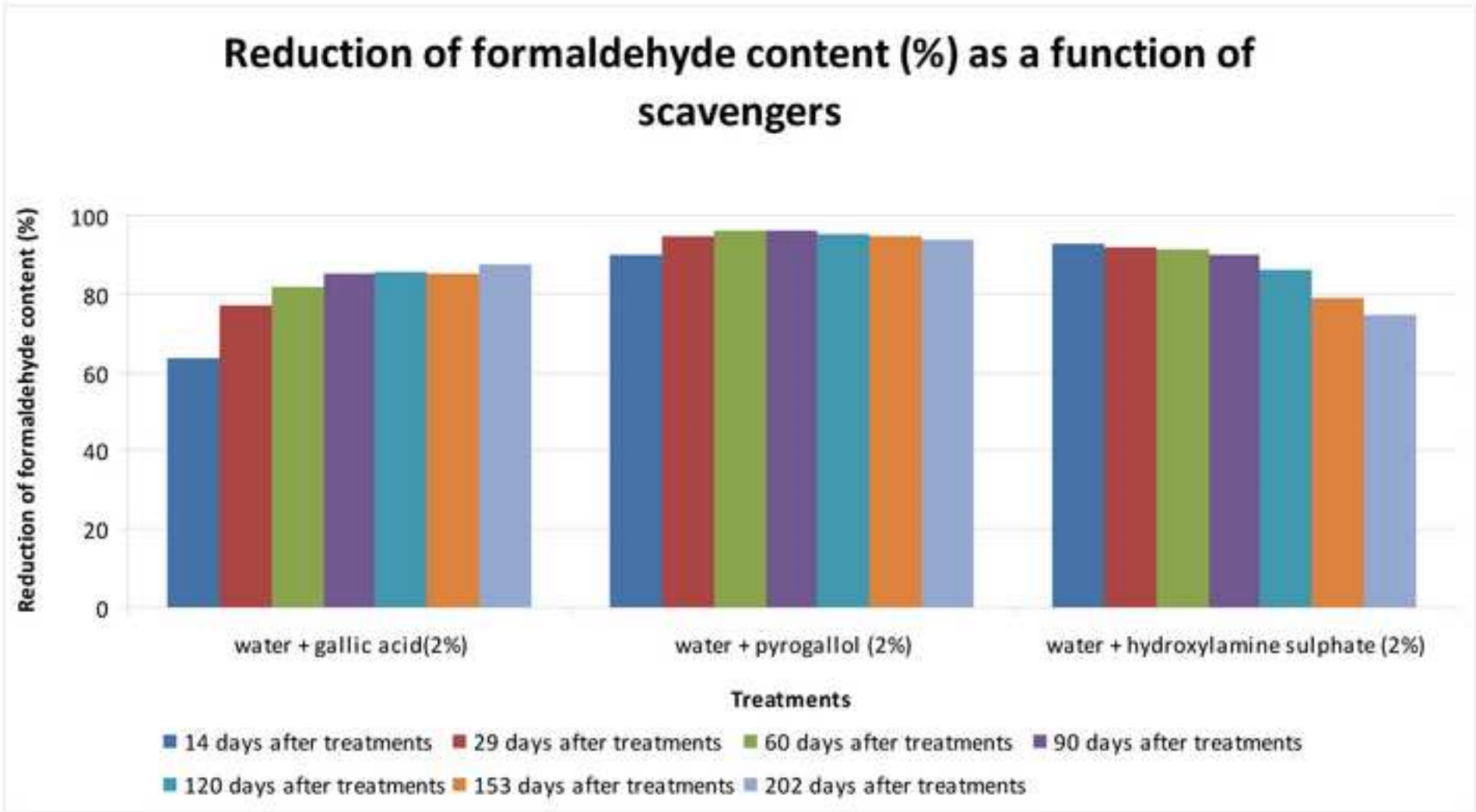


Figure 6
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Formaldehyde content (mg/kg)

Joint effect on formaldehyde content

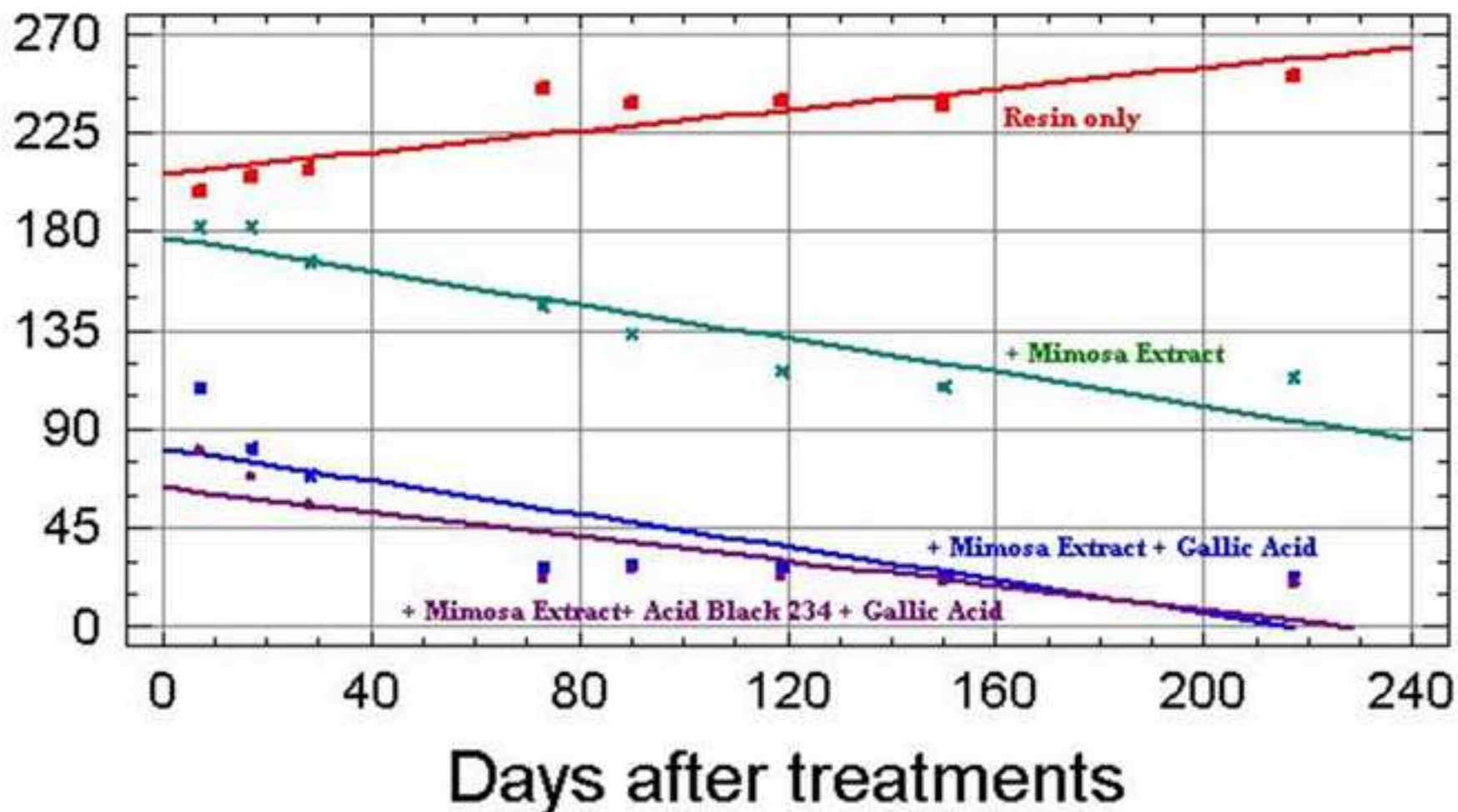


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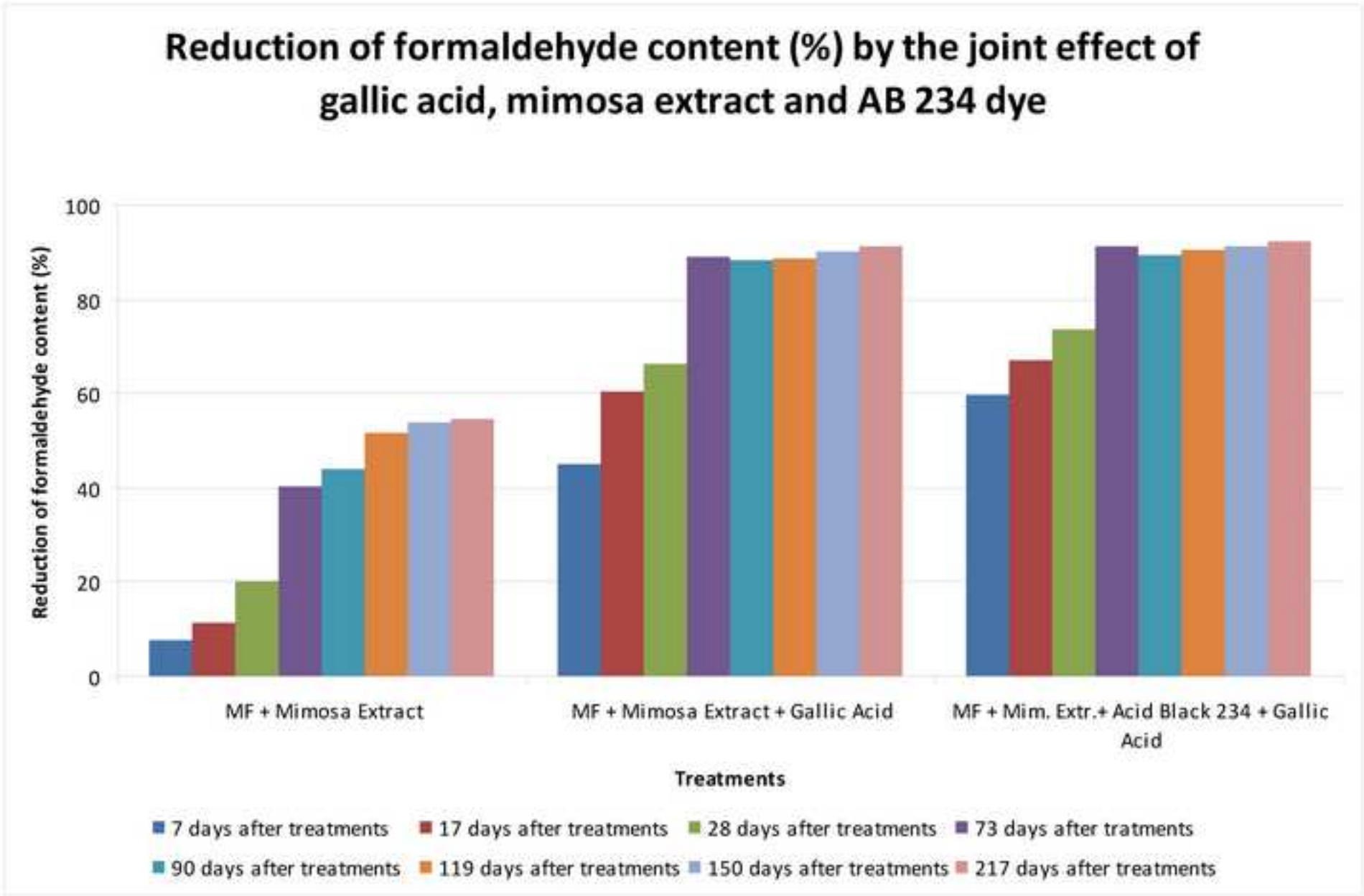


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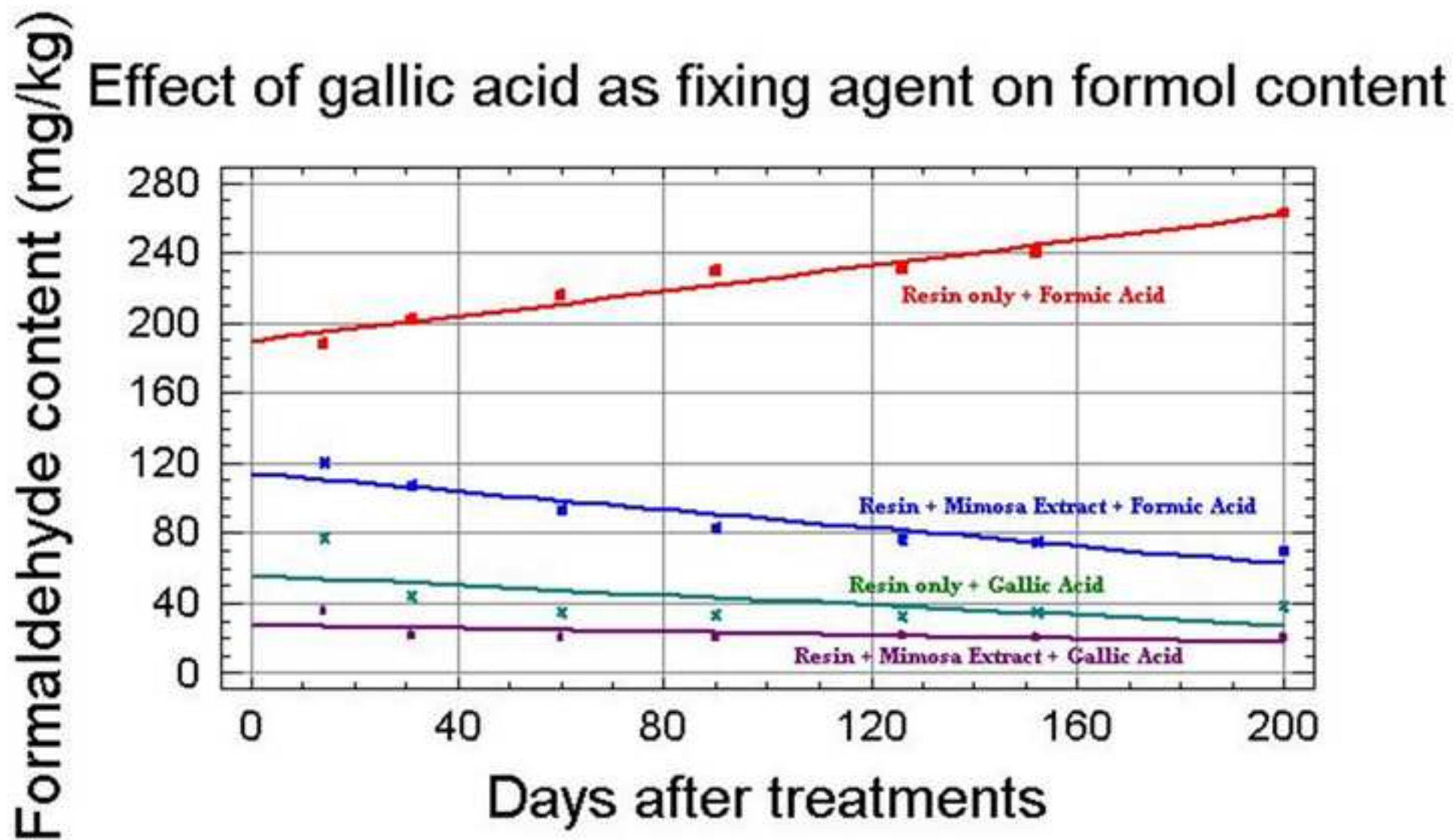


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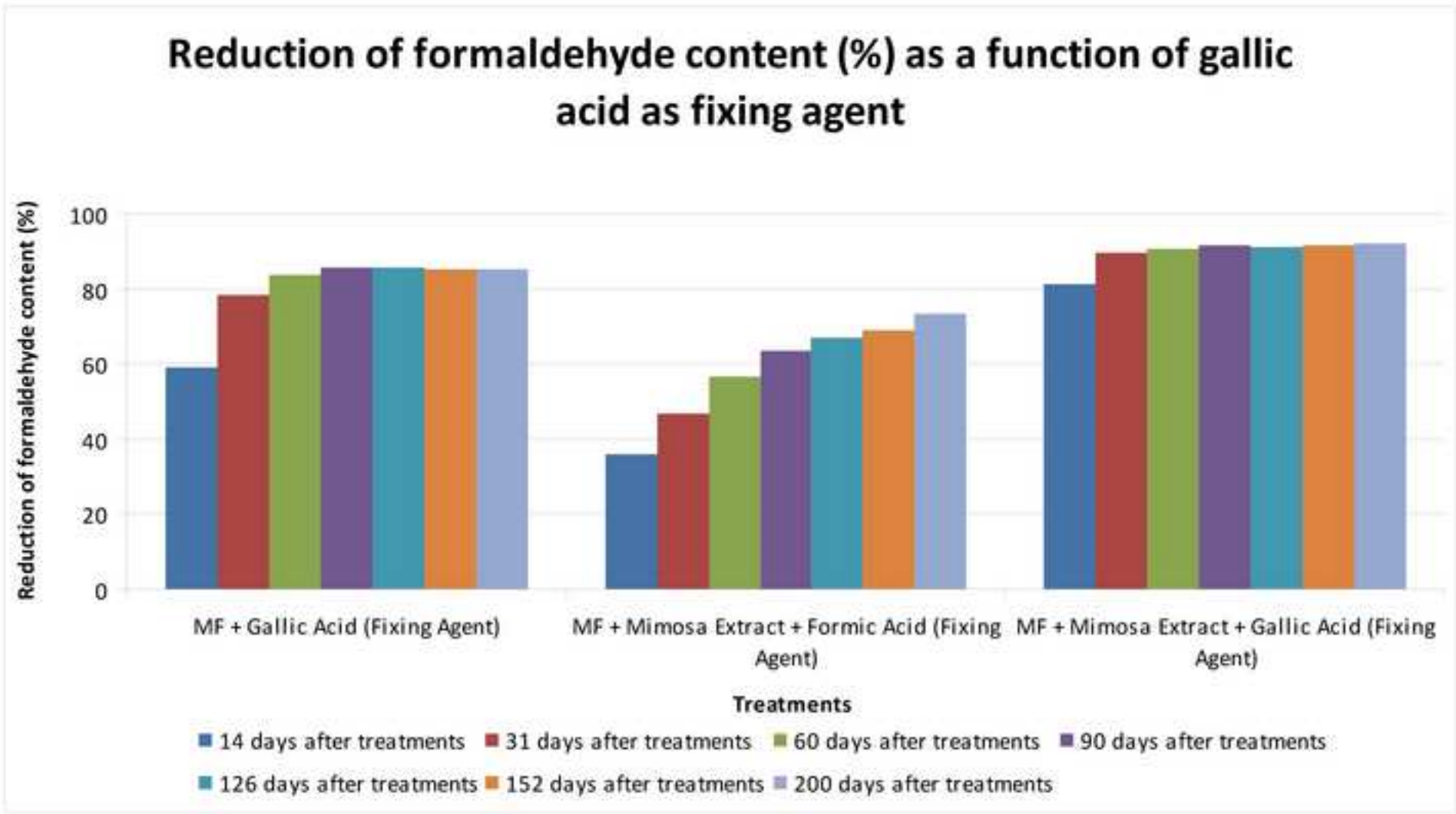


Table 1
Regression equations of formaldehyde content [FC] as a function of the number of days after treatment ND, according to the equation $[FC] = [FC]_0 + [FC]_{rate} \times ND$, including the 95% Confidence Interval for both $[FC]_0$ y $[FC]_{rate}$ for different formaldehyde scavengers used in the final wash.

Regression lines	Resin used	Scavengers used in the final wash	$[FC]_0$ (mg/kg)	$[FC]_{rate}$ (mg/kg)	r
Fig. 2	MF	Water	210.19±16.99	+0.08±0.12	0.6267
		Water + Pyrogallol (2%)	109.54±49.60	-0.47±0.35	-0.8379
		Water + Ethylenurea (2%)	100.16±19.92	-0.18±0.14	-0.8191
		Water + Hydroxylamine Sulphate (2%)	48.75±32.13	+0.02±0.23	0.0864
Fig. 4	DCDF	Water	159.65±14.23	+0.17±0.13	0.7957
		Water + Gallic Acid (2%)	53.77±14.43	-0.19±0.13	-0.8159
		Water + Pyrogallol (2%)	10.51±5.99	-0.01±0.05	-0.1479
		Water + Hydroxylamine Sulphate (2%)	7.46±5.06	+0.18±0.05	0.9682

MF: Melamine-Formaldehyde; DCDF: Dicyandiamide-Formaldehyde
Final wash: 100 % water, 45 min; 45°C

Table 2

Regression equations of formaldehyde content [FC] as a function of the number of days after treatment ND, according to the equation $[FC] = [FC]_0 + [FC]_{rate} \times ND$, including the 95% Confidence Interval for both $[FC]_0$ y $[FC]_{rate}$. Joint effect of gallic acid, mimosa extract and Acid Black 234 dye.

Regression lines	Treatments	$[FC]_0$ (mg/kg)	$[FC]_{rate}$ (mg/kg)	r
Fig. 6	MF (5%) (short wash)	206.54±16.52	+0.24±0.15	0.8496
	MF (5%) + Mimosa Extract (3%) (short wash)	177.20±18.45	-0.38±0.17	-0.9169
	MF (5%) + Mimosa Extract (3%) + Gallic Acid (2%) (long wash)	81.26±29.62	-0.37±0.27	-0.8141
	MF (5%) + Mimosa Extract (3%) + Acid Black 234 (4%) + Gallic Acid (2%) (long wash)	63.52±21.48	-0.28±0.19	-0.8205

MF: Melamine-Formaldehyde; Gallic Acid used in the final wash

Short wash: 150% water; 3 min at room temperature

Long wash: 100% water; 45 min at 45°C

Table 3

Regression equations of formaldehyde content [FC] as a function of the number of days after treatment ND, according to the equation $[FC] = [FC]_0 + [FC]_{rate} \times ND$, including the 95% Confidence Interval for both $[FC]_0$ y $[FC]_{rate}$. Potential use of gallic acid in the final fixing operation of leather processing.

Regression lines	Treatments	$[FC]_0$ (mg/kg)	$[FC]_{rate}$ (mg/kg)	r
Fig. 8	MF (5%) + Formic Acid (2%) (short wash)	189.55±10.13	+0.36±0.09	0.9781
	MF (5%) + Gallic Acid (2%) (short wash)	55.70±25.19	-0.13±0.22	-0.5888
	MF (5%) + Mimosa Extract (4%) + Formic Acid (2%) (short wash)	114.30±12.98	-0.26±0.11	-0.9348
	MF (5%) + Mimosa Extract (4%) + Gallic Acid (2%) (short wash)	27.09±9.33	-0.05±0.08	-0.5498
MF: Melamine-Formaldehyde; Gallic Acid used as fixing agent				
Short wash: 150% water; 3 min at room temperature				